

# Interfacial Tension of Polycaprolactone/Polystyrene Blends by the Imbedded Fiber Retraction Method

G. BIRESAW, C. J. CARRIERE

Biomaterials Processing Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University St, Peoria, Illinois 61604

*Received 9 June 2001; accepted 16 June 2001*

**ABSTRACT:** Polycaprolactone (PCL) is a biodegradable polyester that is widely used in blends with synthetic and natural polymers for various applications. PCL is blended with biopolymers such as starch to improve its wet mechanical properties without impairing the biodegradability and other useful properties of starch. In spite of its importance, little is known about the interfacial tension of PCL blends. Indirect estimates of the room-temperature interfacial tension of PCL blends using wettability methods have been reported. However, direct measurements of the interfacial tension of PCL blends have not been achieved until now, mainly because of the unsuitability of existing equilibrium methods for measuring the interfacial tension of high viscosity blends. We have measured the interfacial tension of PCL/PS blends using the imbedded fiber retraction (IFR) method. The IFR is a dynamic method that allows for the measurement of interfacial tension of high viscosity polymer blends in a relatively short period of time. The interfacial tension of PCL/PS blends was measured from 160 to 200°C. In this temperature range, the interfacial tension of PCL/PS blends is independent of temperature and has a value of  $7.6 \pm 1.8$  dyn/cm. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 3145–3151, 2002; DOI 10.1002/app.10178

**Key words:** polycaprolactone; polystyrene; polymer blends; interfacial tension; imbedded fiber retraction

## INTRODUCTION

Polycaprolactone (PCL) is a synthetic polyester obtained by the self-condensation of the cyclic ester  $\epsilon$ -caprolactone.<sup>1</sup> PCL has unique properties that make it attractive for biomaterials applications. Like most synthetic polymers, it has excellent water-resistant properties. At the same time, like most natural polymers, it has excellent bio-

degradability and biocompatibility properties. These properties have made it possible for PCL to be used in a variety of biomaterial applications including drug release,<sup>2</sup> medical devices,<sup>3</sup> cell cultivation/cell culture,<sup>4</sup> and biodegradable packaging materials.<sup>5</sup>

Manufacture of cost-competitive biomaterials requires that PCL be blended with cheaper synthetic and/or natural polymers. PCL is blended with synthetic polymers to impart biocompatibility and/or biodegradability.<sup>2</sup> On the other hand, PCL is blended with natural polymers, such as starch, to improve their water-resistance properties without impairing their biodegradability/biocompatibility properties.<sup>5</sup> To obtain useful blends, it is important that PCL be compatible with the synthetic and or natural polymers with which it is

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

Correspondence to: G. Biresaw (biresawg@ncaur.usda.gov).

*Journal of Applied Polymer Science*, Vol. 83, 3145–3151 (2002)  
© 2002 John Wiley & Sons, Inc.

blended. One of the factors that determine compatibility is interfacial energy.<sup>6</sup> Various factors influence the interfacial energy of polymer blends, including the surface energy and other properties of blend components.<sup>7,8</sup>

In spite of its importance, little is known about the interfacial tension of PCL blends. Estimates of the room temperature surface energy parameters of PCL from wettability methods have been reported.<sup>3,9–12</sup> Other than an indirect estimation of the room temperature interfacial tension of PCL/starch blends using wettability methods,<sup>12</sup> there are no reports of direct or indirect interfacial tension measurements involving PCL blends with synthetic or natural polymers. Direct measurement of the interfacial tension of PCL blends with synthetic or natural polymers have not been achieved until now, mainly because of difficulty of measuring the interfacial tension of high molecular weight and high viscosity polymer blends by current equilibrium methods, such as sessile or pendant drop methods. In this work, we used the imbedded-fiber retraction (IFR) method<sup>13–16</sup> to overcome this limitation and determine the interfacial energy of PCL/PS blends. IFR is a dynamic method that is particularly suitable for the measurement of the interfacial tension of high molecular weight and high viscosity polymer blends in a relatively short period of time. IFR has been used to measure the interfacial tension of several polymer blends.<sup>13–16</sup> The IFR method involves interfacial tension measurement from the analysis of the microscopic shape change of a fiber of one polymer embedded in a matrix of a second polymer.

Using the IFR method, the interfacial tension of PCL/PS blends was directly measured for the first time at 160, 180, and 200°C. The measured interfacial tensions were then compared with that calculated from the reported room temperature surface energy parameters of PCL and PS. The comparison showed the IFR measured interfacial tensions of PCL/PS to be within the range of the calculated values.

## EXPERIMENTAL

### Materials

Polystyrene samples (Styron 685D) and PCL (PCL 787) were obtained from The Dow Chemical Company and Union Carbide, respectively, and used without further modification.

### Fiber Fabrication

The PS fiber was produced at The Dow Chemical Company with an Instron capillary rheometer, which had been modified to run at low shear rates to avoid orientation and die swell. Prior to fiber fabrication, the PS materials were dried for 24 h under vacuum (<10 mmHg) at 10°C above its glass transition temperature. A temperature-controlled die with a diameter of 0.10 mm was used to extrude PS fibers of the same diameter at  $200 \pm 2^\circ\text{C}$ .

### Matrix Fabrication

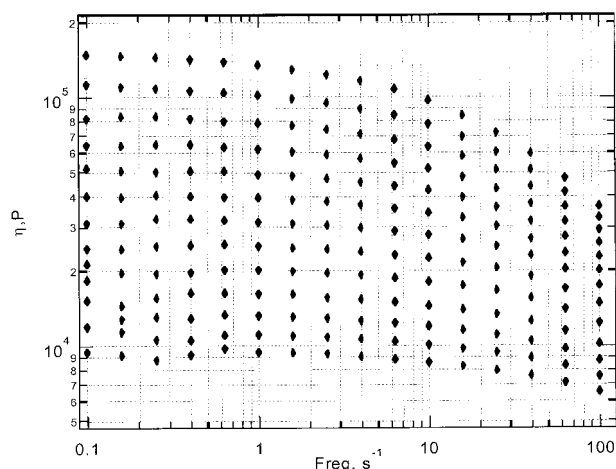
PCL films of  $5 \times 5 \times 0.0625''$  were compression molded on a Carver laboratory press (Wabash, Indiana) equipped with a water-cooling system. The films were then cut into 0.5" diameter discs on a precision CO<sub>2</sub> laser-cutting machine (Kern Electronics & Lasers, Inc; Wadena, MN) for use in IFR experiments. The discs were dried under vacuum at room temperature for at least 24 h prior to use in IFR experiments.

### Zero-Shear Viscosity Measurements

The zero-shear viscosity of the PS and PCL materials was determined with a Rheometrics ARES Series IV dynamic mechanical spectrometer operating under Rheometrics Orchestrator 6.4.4 software. The zero-shear viscosity of PS was obtained as explained elsewhere.<sup>16</sup> The zero-shear viscosity of the PCL samples was measured using 25 mm parallel plate geometry. Frequency/temperature sweep experiments were performed in temperature ranges 80–200, 140–200, and 80–120°C, with steps of 5°C, and a frequency range of 0.1 to 100 rad/s, with data collected at 5 points/decade. As shown in Figure 1, PCL displayed a non-Newtonian behavior, and its zero-shear viscosity at each temperature was obtained by fitting the data to a Carreau model.<sup>17</sup> These computed zero-shear viscosities of PCL followed an Arrhenius dependence on temperature, with an activation energy of  $3.56 \pm 0.06$  kcal/mol. The Arrhenius plot is shown in Figure 2. The values of the zero-shear viscosities of PS and PCL samples used in the IFR experiments are summarized in Table I. The values for the PCL samples were calculated using the activation energy already given. The values for the PS sample have been previously reported.<sup>16</sup>

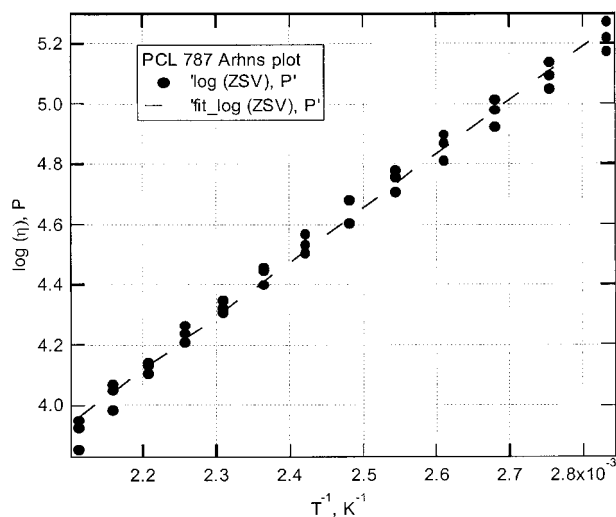
### Thermal Stability of Materials

The PS sample used in this study is stable over the time, and temperatures of the IFR experi-



**Figure 1** Dynamic frequency/temperature sweep of PCL (80–200°C).

ments and the procedure used to evaluate its thermal stability have been described elsewhere.<sup>16</sup> The thermal stability of PCL was determined at 160, 180, and 200°C by examining the magnitude of the complex viscosity as a function of time with a Rheometrics ARES Series IV dynamic mechanical spectrometer equipped with 25-mm parallel plate geometry. The resulting time–viscosity profile showed an initial stable region followed by a region of sharp decrease in viscosity. The durations of the initial stable regions were ~ 5.5, 2.0, and 0.5 h at 160, 180, and 200°C, respectively, which are longer durations than those of the IFR experiments at these tem-



**Figure 2** Arrhenius dependence of zero-shear viscosity for PCL.

**Table I** Zero Shear Viscosities of Polymers at IFR Temperatures, *P*

Temp, °C	PCL	PS <sup>a</sup>
160	$2.05 \pm 0.310 \times 10^4$	$6.10 \pm 0.6 \times 10^6$
180	$1.34 \pm 0.195 \times 10^4$	$7.70 \pm 0.1 \times 10^5$
200	$9.16 \pm 1.27 \times 10^3$	$1.80 \pm 0.2 \times 10^5$

<sup>a</sup> From ref. 16.

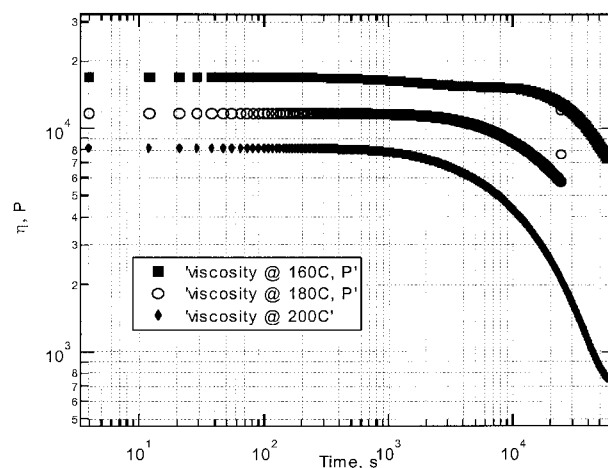
peratures. Thus, PCL is thermally stable for the duration of the IFR experiments at these temperatures. The effects of time and temperature on the viscosity of PCL are illustrated in Figure 3.

### The IFR Instrument

The IFR apparatus used in this work has been described elsewhere.<sup>16</sup> Its main components are an oven for maintaining the sample at the required temperature to  $\pm 0.1^\circ\text{C}$ , an optical system for viewing the sample, and a digital image recorder (Sony DKR700) for recording the retraction process. The digital still recorder can be programmed to record images at any interval between 30 s and 1 h.

### Interfacial Tension Measurement

Latex gloves were used to handle fiber and matrix materials during all manipulations. The fibers were cut with a surgical scalpel into 1–2-mm-long samples that were kept at 100°C under vacuum for at least 24 h prior to use. The length and diameter of the fibers were measured at room



**Figure 3** Effect of temperature on the stability of PCL at 160–200°C.

temperature with a travelling microscope. The fiber was then placed between PCL disks and placed in the sample holder of the IFR oven. The fiber was entombed in the matrix material at 20–40°C below the retraction temperature. After the melt front had closed around the fiber, the sample was annealed for few more hours to ensure the elimination of any residual stress that might have been generated during fiber fabrication. After the annealing process, the oven temperature was raised to the retraction temperature, and the image of the fiber was recorded at a suitable time interval until the fiber was completely transformed into a sphere. The fiber dimensions were then measured from the images as a function of time and used to calculate the interfacial tension.

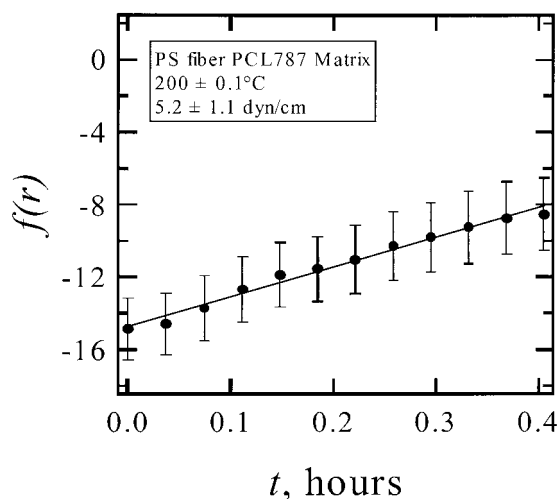
## RESULTS AND DISCUSSION

### The IFR Method

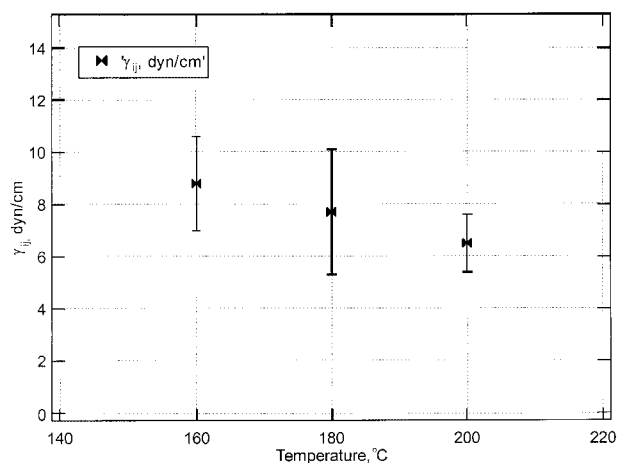
In the IFR method, a fiber of polymer A with an initial radius of  $R_e$  is imbedded in a matrix of polymer B. The retraction of the fiber at the desired temperature is monitored as a function of time until the fiber is transformed into a sphere of radius  $R_0$ . From the retraction images, a shape function,  $f(r)$ , is calculated. A linear relationship exists between the shape function  $f(r)$  and the retraction time  $t$  as follows (eq. 1):

$$f(r) = f(r_e) + (\gamma_{12}/\eta R_0)t \quad (1)$$

where  $f(r_e)$  is the shape function at  $t = 0$ .



**Figure 4** Typical  $f(r)$  versus  $t$  plot for PCL/PS blend.



**Figure 5** Effect of temperature on the interfacial tension of PCL/PS blend measured by the IFR method.

The interfacial tension,  $\gamma_{12}$ , is calculated from the slope of  $f(r)$  versus  $t$  plot and the independently determined zero shear viscosities of the fiber and matrix materials at the retraction temperature (eq. 2):

$$\gamma_{12} = (\text{slope})\eta R_0 \quad (2)$$

where:

$$\eta = (\eta_m + 1.7\eta_f)/2.7$$

and  $\eta_m$  and  $\eta_f$  are the zero-shear viscosities of the matrix and fiber, respectively. Details of the IFR theory and derivation of the pertinent equations are given elsewhere.<sup>13–16</sup> As an example, a typical  $f(r)$  versus  $t$  plot for a PCL/PS blend at 200°C is shown in Figure 4.

### Interfacial Tension of PCL/PS Blends from IFR Measurements

The interfacial tension of PCL/PS blends was measured at 160, 180, and 200°C. Four measurements were taken at each temperature, and the average of the four measurements  $\pm$  one standard deviation is shown in Figure 5. As shown in Figure 5, the interfacial tension appears to decrease with increasing temperature. This result is similar to observations on most polymer blends.<sup>7,8</sup> However, when one takes into account the standard deviations, the interfacial tension could be considered to be independent of temperature. This lack of temperature dependence of the interfacial tension of blends is rare but has been ob-

**Table II** Comparison of IFR Measured Versus Calculated<sup>a</sup> PCL/PS Interfacial Energies

Temp, °C	PCL Surface Energy Parameters, dyn/cm			Interfacial Energy, dyn/cm		
	$\gamma^D$	$\gamma^P$	Ref.	Calc, GM <sup>b</sup>	Calc. HM <sup>c</sup>	Meas, IFR <sup>d</sup>
Ambient	24.4	2.1	9	2.4	4.7	
Ambient	32.1	2.0	9	0.9	1.6	
Ambient	35.2	10.3	10	6.1	9.0	
Ambient	37	7	10	3.6	5.5	
Ambient	41.9	6.4	3	3.1	4.8	
Ambient	45.2	0.3	11	0.2	0.4	
160						8.8 ± 1.8
180						7.7 ± 2.4
200						6.5 ± 1.1
160–200						7.6 ± 1.8

<sup>a</sup> PS surface energy parameters (from ref. 7), dyn/cm:  $\gamma^D = 40.1$ ,  $\gamma^P = 0.6$ .

<sup>b</sup> Geometric mean (eq. 3).

<sup>c</sup> Harmonic mean (eq. 4).

<sup>d</sup> This work, by the imbedded fiber retraction method.

served for a very small number of polymer blends.<sup>7,8</sup> Another reason for the insensitivity of the interfacial tension to temperature might be the relatively narrow range of temperature used in this study. The observed reduction in the average interfacial tension shown in Figure 5 was within the measurement error of the IFR method, which is in the range of  $\pm 20\%$ . We were unable to increase the temperature range of the experiment: below 160°C, the PCL did not sufficiently melt to conduct the retraction experiment, and above 200°C, the retraction process was too fast to measure.

#### Interfacial Tension of PCL/PS Blends from Surface Energy Parameters

The interfacial energy of polymer blends ( $\gamma_{ij}$ ) can be calculated from the known dispersive ( $\gamma^D$ ) and polar ( $\gamma^P$ ) surface energy parameters of blend components using the geometric mean (GM) or harmonic mean (HM) expressions shown in eqs. 3 and 4, respectively<sup>7,8</sup>:

$$\gamma_{ij} = \gamma_i + \gamma_j - 2[\gamma_i^D \gamma_j^D]^{0.5} - 2[\gamma_i^P \gamma_j^P]^{0.5} \quad (3)$$

$$\gamma_{ij} = \gamma_i + \gamma_j - 4[\gamma_i^D \gamma_j^D][\gamma_i^P + \gamma_j^P] - 4[\gamma_i^P \gamma_j^P][\gamma_i^D + \gamma_j^D] \quad (4)$$

where  $i$  and  $j$  are blend components;  $\gamma_i = \gamma_i^D + \gamma_i^P$ ; and  $\gamma_j = \gamma_j^D + \gamma_j^P$ .

Reported room temperature dispersive and polar surface energy parameters of PS are 40.1 and

0.6 dyn/cm, respectively.<sup>7</sup> Six sets of dispersive and polar surface energy parameters have been reported for PCL at room temperature using wettability methods,<sup>3,9–11</sup> and these values are summarized in Table II. The interfacial energy of the PCL/PS blend was calculated using the aforementioned surface energy parameters of PS with each set of PCL surface energy parameters. The calculations were carried out using both the GM (eq. 3) and HM (eq. 4) approximations. The results are summarized and compared with measured values from the IFR experiments of this work in Table II.

Examination of Table II shows that calculated room temperature PCL/PS interfacial energies were in the range 0.2–6.1 and 0.4–9.0 dyn/cm for the GM and HM approximations, respectively. The IFR measured value is  $7.6 \pm 1.8$  dyn/cm and is independent of temperature in the range 160–200°C. If we assume that the interfacial tension of PCL/PS blend is independent of temperature all the way to ambient temperatures, then the IFR measured interfacial tension values will be in the range predicted by both the GM and the HM equations. However, it appears that the IFR measured values were closer to the high end of the values from the HM than those from the GM approximations.

#### CONCLUSION

PCL is a synthetic polyester obtained by the self-condensation of the cyclic ester  $\epsilon$ -caprolactone. Its

excellent water-resistant, biodegradability and/or biocompatibility properties has made it possible for PCL to be used in a variety of biomaterial applications, including drug release, medical devices, cell cultivation/cell culture, and biodegradable packaging materials. Manufacture of cost-competitive biomaterials requires that PCL be blended with cheaper synthetic and/or natural polymers. However, to obtain useful biomaterial blends, it is important that PCL be compatible with the synthetic and/or natural polymers with which it is blended. One of the factors that determine compatibility is interfacial energy, which is a function of various parameters, including the surface energy and other properties of blend components.

In spite of its importance, little is known about the interfacial tension of PCL blends. Other than an indirect estimation of the room temperature interfacial tension of PCL/starch blends using wettability methods, there are no reports of direct or indirect interfacial tension measurements involving PCL blends with synthetic or natural polymers. Direct measurement of the interfacial tension of PCL blends with synthetic or natural polymers has not been achieved until now, mainly because of difficulty of measuring the interfacial tension of high molecular weight and high viscosity polymer blends by currently available equilibrium methods, such as sessile or pendant drop methods. This problem has now been overcome with the use of the IFR method. IFR is a dynamic method that is particularly suitable for the measurement of the interfacial tension of high viscosity and high molecular weight polymer blends in a relatively short period of time. IFR has been used to measure the interfacial tension of several polymer blends. The IFR method involves interfacial tension measurement from the analysis of the microscopic shape change of a fiber of one polymer embedded in a matrix of a second polymer.

In this work, the IFR method was used to directly measure, for the first time, the interfacial tension of PCL/PS blends at 160, 180, and 200°C. The interfacial tension at each temperature was obtained from the average of four measurements. The result showed the average interfacial tension decreasing with increasing temperature, which is typical of most polymer blends.<sup>7,8</sup> However, when one takes into account the standard deviations, the interfacial tension becomes independent of temperature in the temperature range studied, with a value of  $7.6 \pm 1.8$ . This lack of temperature dependence of the interfacial tension of blends is

rare but has been observed for a very small number of polymer blends.<sup>7,8</sup> Another reason for the insensitivity of the interfacial tension to temperature might be the relatively narrow range of temperature used in this study. The observed reduction in the average interfacial tension was within the measurement error of the IFR method, which is in the range of  $\pm 20\%$ . We were unable to increase the temperature range of the experiment.

The interfacial tension of PCL/PS was also calculated from the reported room temperature dispersive and polar surface energy parameters of PS and PCL. These values for PS were 40.1 and 0.6 dyn/cm, respectively. However, six sets of dispersive and polar surface energy parameters have been reported for PCL. The calculations were carried using the aforementioned surface energy parameters of PS with each set of PCL surface energy parameters by the geometric mean (GM) and harmonic mean (HM) approximations. The result shows that calculated room temperature PCL/PS interfacial energies were in the range 0.2–6.1 and 0.4–9.0 dyn/cm for the GM and HM approximations, respectively. The IFR measured interfacial tension values of  $7.6 \pm 1.8$  dyn/cm, assuming it to be independent of temperature all the way to ambient conditions, are in the range predicted by both the GM and the HM equations. However, it appears that the IFR measured values were closer to the high end of values from the HM than that from the GM approximations.

The authors thank J. Anderson, A. R. Loffredo, A. J. Lulay, and A. J. Thomas for their help with sample preparation and obtaining the viscosity and interfacial tension data; and Dr. E. B. Bagley for reviewing and commenting on this manuscript. This work was supported by USDA.

## REFERENCES

1. "Tone® Polymers" Union Carbide Corporation, 1988.
2. Bei, J.; Wang, W.; Wang, Z.; Wang, S. *Polym Adv Technol* 1966, 7, 104.
3. Yasin, M.; Tighe, B. *J Biomaterials* 1992, 13, 9.
4. Rouxhet, L.; Duhoux, F.; Borecky, O.; Legras, R.; Schneider, Y. *J Biomater Sci, Polym Ed* 1998, 9, 1279.
5. Koenig, M. F.; Huang, S. J. *Polymer* 1995, 36, 1877.
6. Vanoene, H. *J Colloid Interface Sci* 1972, 40, 448.
7. Wu, S. *Polymer Interface and Adhesion*; Dekker: New York, 1982.

8. Owen, M. J. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed., AIP Press: New York, 1996, Chapter 48.
9. Erbil, H. Y.; Yasar, B.; Suezer, S.; Baysal, B. M. *Langmuir* 1997, 13, 5484.
10. Normand, F.; Granier, A.; Leprince, P.; Marec, J.; Shi, M. K.; Clouet, F. *Plasma Chem Plasma Process* 1995, 15, 173.
11. Biresaw, G.; Carriere, C. J. *J Polym Sci B: Polym Phys* 2001, 39, 920–930.
12. Lawton, J. W. In *Cereals: Novel Uses and Processes* [Proc. Int. Conf.; Meeting Date 1996]; Campbell, M.; Webb, C.; McKee, S. L.; Eds., Plenum Press: New York, 1997, 43.
13. Carriere, C. J.; Cohen, A.; Arends, C. B. *J Rheol* 1989, 33, 681.
14. Cohen, A.; Carriere, C. J. *Rheol Acta* 1989, 28, 223.
15. Carriere, C. J.; Cohen, A. *J Rheol* 1991, 35, 205.
16. Carriere, C. J.; Biresaw, G.; Sammler, R. L. *Rheol Acta* 2000, 39, 476.
17. Bird, R. B.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids*, vol 1, 2<sup>nd</sup> ed.; Wiley: New York, 1987.